Influence of fillers on mechanical properties of ATH filled EPDM during ageing by gamma-irradiation

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Abstract:

The influence of the presence of fillers in the degradation mechanisms and on the evolution of the mechanical properties is studied with ATH filled EPDM. The presence of an important fraction of fillers accelerates the degradation process under irradiation. Above the melting temperature of the EPDM, this induces a decrease in the apparent mechanical reinforcement of the fillers. This also promotes decohesion mechanisms which enables an increase in the strain at break with irradiation dose, conversely to the decrease in the strain at break observed for unfilled matrix. The use of a filler treatment does not seem to modify the acceleration effect of the filler on the degradation. However the consequence is to delay the appearance of decohesion mechanisms. At room temperature, i.e. below the melting temperature, all the consequences of ageing by gamma-irradiation for the range of irradiation doses tested are strongly attenuated by the presence of a semi-crystalline microstructure, the morphology of which being not too strongly modified by irradiation.

Keywords: Filled rubber, irradiation, mechanical properties

1. Introduction

EPDM rubbers, because of their excellent electrical insulation properties, are widely used in wire and cable coatings. The increasing demand for EPDM in electrical applications is also due to its excellent resistance to degradation and easiness to accept large amounts of fillers. Thus formulations which used aluminium trihydroxide (ATH) as fillers with good mechanical and ageing resistance, with flame retardancy and smoke suppression characteristics have been developed. These polymer materials used in cables and accessories can be exposed to severe environmental conditions. An example would be cables in nuclear power plants which may be exposed to elevated temperatures and gamma irradiation. These conditions are known to cause their ageing and consequently their degradation over time. Ageing by gamma irradiation of crosslinked EPDM elastomers has been studied for unfilled rubbers [1, 2, 3, 4, 5]. Chain scissions and crosslinking mechanisms have been evidenced, depending on the irradiation conditions and on the polymer formulation.

However, the influence of fillers such as ATH on the degradation mechanisms and then its consequences on the mechanical properties have been scarcely investigated [6, 7, 8]. Nevertheless, fillers can influence the degradation mechanism. They can modify the polymer degradation by trapping radicals or degradation by-products which can interact with intermediate chemical species involved in the matrix degradation. They can also be degraded and lead to the formation of supplementary degradation by-products, which can interact with the matrix degradation process. Moreover, whether they are still inert or not during the matrix degradation, this matrix degradation can induce a modification of the filler-matrix interaction: this may have consequences in the reinforcement efficiency of the filler, and therefore be involved in the consequences of the degradation in the overall properties of the composite. For instance, the study of the photo-oxidation of EPDM filled ATH [8] has shown different

changes of stress and elongation at break for filled and unfilled samples which were assigned to the modification of the filler-matrix interactions.

In addition, the semi-crystalline state of the studied EPDM must be taken into account. Indeed, as reported in literature, fillers can modify the crystallinity of composites and they can form a mixed network with crystallites. This structure induces a large reinforcement efficiency [10]. Moreover in a previous study it has been shown that the crystallite presence in an unfilled EPDM limits the consequences of irradiation on the mechanical properties in the semi-crystalline state [11]. When these filled materials are aged by gamma irradiation, the evolution of the crystalline microstructure can be different than that observed for unfilled matrix. For example, more recently, it was found that the low flux of neutron promotes in ATH filled EDPM the growth of crystalline zones [12], which leads to an increase in the elastic modulus [13].

Thus, in this paper, it is proposed to study the effect of the presence of ATH filler on the evolution of the mechanical properties of ATH filled crosslinked EPDM after ageing by gamma irradiation at room temperature. Since the filler-matrix interaction seems to play a crucial role during ageing, formulations with coupling agent are also investigated. In addition, uncrosslinked formulations have also been studied to have better insight on the degradation process. At last, in order to understand the role of the semi-crystalline phase, the consequences of ageing on the mechanical properties are studied both in the rubbery state (i.e. at 80°C) and in the semi-crystalline state (at room temperature).

2. Experimental

2.1. Materials

The EPDM elastomer studied (Nordel IP NDR 3722 P from Dow Chemical Company) contains 70% ethylene, 29.5% propylene and 0.5% ENB. The crosslinking agent is the

dicumyl peroxide (Perkadox BC-FF from Akzo Nobel). EPDM is filled with ATH, which is a micronic filler of an average size of 1.3µm meaning a specific surface area of 3.5m^2/g. The basic structure forms stacked sheets of linked octahedrons of aluminum hydroxide. The hydroxides can be assimilated to crystal water. Generally, there is free bound water at the filler surface [14, 15]. This filler is an anti-flame agent: during thermal degradation, it undergoes endothermic dehydration releasing water, which leads to formation of a thermally stable ceramic material, i.e. alumina trihydroxide Al_2O_3. The formation of a surface layer of Al_2O_3 acts as a shield to heat and mass transfer between the polymer and the flame. Two types of ATH have been chosen for this study: ATH without surface treatment (Apyral 40CD from Nabaltec) and ATH surface treated with a vinylsilane (Apyral 40VS1 from Nabaltec). This surface treatment is made of a reactive foot with three ethoxy groups, which react with the silanol of the filler surface, and an alkyl chain with a vinyl function, which can react with the matrix during crosslinking. The silane treatment is done to improve the filler-matrix interactions [16, 17]. The treated ATH will be named hereafter ATHT and the untreated one ATHU.

The compositions of the different formulations and their name can be found in Table 1. For the uncrosslinked formulations, only one type of filler: ATHU and one filler ratio has been studied: 150 phr, that is 150 weights ratios for 100 weight ratios of EPDM, which corresponds to a weight fraction of 60% and a volume fraction of 35%. For the crosslinked rubbers, two ATHU ratios have been studied: 32 phr, which corresponds to a weight fraction of 24% and a volume fraction of 10% and 150 phr. The material based on treated ATH is crosslinked and the filler content is 150 phr (E-CR-150ATHT).

The samples are processed following three steps. The first step is the mixing of the matrix and the incorporation of fillers and crosslinking agent in the polymer. First the matrix is introduced in the internal mixer and mixed for 2 minutes, and then the fillers are introduced.

If the elastomer has to be crosslinked, peroxide is added after 5 minutes of mixing, its dispersion is obtained after mixing 10 min, at low temperature (80°C) to prevent any reaction of the crosslinking system. In order to obtain a better filler dispersion, the second step is the mixing in an external mixer (cylinders) for 10 min at low temperature (80°C). During the last step, the compound is pressed as 1-mm-thick films at 170 °C to promote crosslinking reaction. For the crosslinked materials, the curing time (t_{98} at 170°C) is estimated from torque measurement performed with a MOSANTO analyser: the crosslinking is carried out for 10 min (i.e. the same time as for the unfilled material). For the uncrosslinked materials, this time is fixed to 3 min, i.e. the time needed to obtain the sample shape.

2.2. Ageing conditions

All samples are exposed to gamma-radiation of a ^{60}Co source at a dose rate of 1 kGy/h in an oxygen atmosphere for doses 50, 165, 300 and 510 kGy (Arc Nucleart – Grenoble France): the water temperature of the pool, where exposures are performed is about 18°C. Afterwards, they are stored under vacuum at about 22°C. The samples will be named hereafter E-NC-ZZZ, E-NC-XXXATHY-ZZZ, E-CR-ZZZ, E-CR-XXXATHY-ZZZ with XXX the filler ratio, Y for the filler type (U for untreated or T for treated), and ZZZ for irradiation dose.

2.3. Instruments

2.3.1. IR spectroscopy

In order to evaluate the degree of oxidation of the materials, analyses by IR spectroscopy were performed. Firstly, changes in carbonyl concentration were followed by a Thermo Nicolet Nexus FT-IR spectrophotometer with the technique Attenuated Total Reflectance (ATR) accessory using 32 scans and a resolution of 4 cm^{-1}. IR spectroscopy in the transmission mode could not be used because the samples are absorbing. Secondly, oxidation (carbonyl) profiles were deduced from IR-microspectroscopy using a Continuμm microscope

coupled to a Nexus Nicolet optical bench (32 scans, resolution of 4 cm^{-1}). A slice of sample of about 40 µm was cut by cryo-microtom in the thickness direction. Then IR spectra were measured on this slice every 50 µm to have an oxidation profile along the sample thickness. These analysis were conducted in CNEP - Centre National d'Evaluation de Photoprotection – Clermont Ferrand (France).

2.3.2. Swelling measurements

2.3.2.1. Swelling in xylene

The swelling measurements are very useful to characterize the network degradation. In the case of unfilled rubbers, the swelling restriction is due to crosslinks connecting the polymer chains, which avoid their extension and their diffusion. Swelling provides information on the matrix network chain density (determined from the swelling ratio) and the percentage of soluble fraction (i.e. the proportion of chains which do not belong to the network). Because of the filler-rubber interactions, fillers can play the role of additional crosslinks. Besides, their presence, via filler-filler interactions can also restricts the swelling. Therefore it is hazardous to relate the swelling ratio to the matrix network chain density and the results on the measurements will be considered only as qualitative. The swelling procedure is as follows: samples with an initial weight M_i and a filler weight fraction ε are introduced in xylene for 8 days to achieve the swelling equilibrium; then the swollen material with a weight M_s is dried under vacuum at 60°C during 1 day and finally weighted to obtain the dried mass M_d.

The swelling ratio Q of the polymer and the soluble fraction F_s are calculated taking into account the non swelling of the fillers, and the fact that the soluble fraction does not contain fillers (it was checked afterwards for all the samples), from the following relations:

$$Q = 1 + \frac{\rho_{polymer}}{\rho_{xylene}} \frac{M_s - M_d}{M_d (1 - \varepsilon)} \quad (1)$$

$$F_s = \frac{M_i - M_d}{M_i - \varepsilon M_i} \times 100 \quad (2)$$

In the case of filled rubbers, Kraus has developed an empirical approach which enables to characterize the strength of the filler-matrix interactions [18]. Thus, considering the Q/Q_0 ratio, i.e. the composite swelling ratio divided by the unfilled polymer swelling ratio, a value inferior to one suggests good filler matrix-interactions, while a ratio superior to one is significant of bad interactions.

2.3.3. Microscopy

Evidences of good filler dispersion within the matrix were provided by images obtained in an Environnemental Scanning Electron Microscopy (FEI XL 30 FEG ESEM). This ESEM is equipped with a Field Emission Gun which enables observation at low voltage (1 kV), so that sample metallization can be avoided. Prior to their observation, the samples were fractured in liquid nitrogen. The used detector collects secondary electron and the observation of the sample fracture surface is performed in high vacuum.

2.3.4. Tensile tests

Tensile tests are performed on an MTS device. Experiments are conducted at 80°C and at 25°C with a true strain rate 0.01 s^{-1}. An image processing acquisition system (Apollor VideoTraction System) is used to obtain the true stress-true strain curves. The samples are dumbbell-shaped with dimensions 20 x 4 x 1 mm^3. Average stresses and strains at break from three tested samples and error bars are given in figure 12. The elastic modulus E is calculated from the slope of the linear initial portion of the tensile test curve.

Tensile test cycles are also performed at 80°C, i.e. above the crystallite melting temperature. Firstly the sample is stretched up to a true strain of 0.2, relaxed during 5 minutes, then stretched again at a higher true strain; this experiment is repeated with an incremental 0.2 true strain, up to the sample rupture.

2.3.5. Differential scanning calorimetry

All measurements were carried out with a Perkin-Elmer Diamond calorimeter, with 10-15 mg of material encapsulated in a standard aluminum pan. The crystallization temperature domain of our EPDM is large [11]: from about -50°C up to 60°C. A thermal treatment was applied to all samples to obtain a stable crystallinity ratio around 22°C, in particular during the ageing in the pool at 18°C, and the post-irradiation at 22°C:

- A heating ramp up to 80°C to erase the previous thermal history
- A rapid cooling down to the optimal crystallization temperature 22°C and storage during 12h at this temperature.
- A heating ramp of 1°C/min up to 38°C, the temperature at which the samples are maintained during 6h.

Then the samples are cooled down to 22°C and stored at this same temperature. This treatment enables to get a unique well defined melting peak for unfilled EPDM materials and a double peak for ATH filled EPDM. Thus these materials have one or two crystallite populations with melting temperatures above 22°C.

To study the materials cristallinity after their irradiation, they are cooled from room temperature down to –50°C at a cooling rate of 10°C/min and heated up to 100°C at 10°C/min. The cooling from room temperature to -50°C is necessary to avoid a DSC peak overshoot overlapping the melting peaks. However this cooling induces the formation of an additional melting peak, which can be observed between -40°C and 20°C. That is why the crystallinity ratio X_c is defined from enthalpy of the melting peaks between 22°C and 60°C ΔH_f:

$$X_c = \frac{\Delta H_f}{(1-\varepsilon)\Delta H_{f0}} \quad (3)$$

where ε the weight ratio of fillers and ΔH_{f0} is taken equal to 290 J/g [19], i.e. the value for perfect polyethylene crystal, since it is assumed that cristallisation occur only in polyethylene segments.

3. Results

3.1. Preliminary characterization of the non irradiated materials

Table 2 gives the swelling ratios Q, Q_0 and the soluble fraction F_p of the different samples. As said previously, it was checked by thermogravimetric analyses that the sol fractions obtained with filled elastomers do not contain fillers. Both uncrosslinked materials are totally soluble in xylene, even at large filler content (E-NC-150ATHU-0), evidencing the absence of any filler percolating structure. This is expected in the case of micron fillers, which have a low specific surface [20]. Such absence of rigid structure of fillers is also expected in the crosslinked materials.

Concerning these materials, the polymer phase of the filled rubbers (E-CR-150ATHU and E-CR-150ATHT) has a swelling ratio inferior to the matrix one. The ratio Q/Q_0 are given in Table 2. Whatever the materials, they show a ratio below one, significant of some filler-matrix interactions. In E-CR-150ATHU these interactions are probably physical ones. In E-CR-150ATHT, the silane treatment induces additional covalent bonds between the polymer and the filler (all over the filler surface). This is mainly evidenced in swelling experiments (Q/Q_0 is lower) and at large strains, that is when the elastomer matrix is deformed at a significant level [21, 22]. Such effect is also confirmed by the observation of the fracture profile of both materials. Figure 1 shows holes at the surface of E-CR-150ATHU with neat interfaces between fillers and matrix, revealing weak filler-matrix interactions, whereas fracture profile of E-CR-150ATHT looks very different with continuity between the matrix and fillers, suggesting stronger filler-matrix interactions. Moreover it can be noted that E-CR-

150ATHT contains a significant polymer soluble fraction (ca.6%). This can be explained by the fact that a part of the peroxide is used for the coupling reaction between fillers and matrix, leading to a less efficient matrix crosslinking.

It is well known that polymer adsorption on the filler surface leads to a false evaluation of the matrix swelling ratio. Ammonia atmosphere enables to cleave physical linkages between filler and polymer [23, 24, 25, 26] and suppresses the filler influence in the polymer swelling measurements. Ammonia fume treatment was applied to E-CR-150ATHT and E-CR-150ATHU : samples are put in a dessiccator in presence of ammonia fumes during three days. This treatment leads to an increase in E-CR-150ATHU swelling ratio (cf. Q_a in Table 2**)**: this one, corrected of the filler presence, is equal to that of the unfilled matrix E-CR submitted to the same treatment. This, in addition to the absence of sol fraction, suggests that the matrix crosslink density is the same in both materials. Conversely, the ammonia treatment has no significant effect on E-CR-150ATHT swelling ratio. It was expected since the covalent bonds are not affected by the ammonia treatment.

The tensile moduli of the filled and unfilled crosslinked samples are plotted in Figure 4 b. The modulus increase measured with 32 phr of ATH corresponds to a factor of about 1.2. The reinforcement is of the same order as that predicted by the generalized self consistent scheme of Christensen and Lo, [27, 28] which predicts a value of 1.3. (The difference between the theoretical and experimental values is within the experimental uncertainties): This was expected for a composite in which the fillers can be considered as dilute particles. 150 phr of ATH (35vol. %) leads to an experimental reinforcement of a factor around 3.5. This value is slightly higher than the one predicted by Christensen and Lo model, which gives a value of 3.1 (calculation performed with a filler modulus above 1GPa). An explanation could be a higher effective form factor of the filler (which are assumed to be spherical in the Christensen and Lo model), leading to a better reinforcement of the material. Such assumption might be

supported by the lower value found for the reinforcement factor calculated for E-CR-150ATHT, ca.3.2, since the filler treatment is known to promote a better filler desagglomeration; even if this lower reinforcement factor might also be due to the lower initial crosslink density of the matrix of this material. In any case, it can be concluded, that the reinforcement obtained with 150 phr of ATH is of the order of 3.5.

As expected, 32 phr of untreated ATH induces a very slight increase in stress, with a negligible variation of the ultimate properties (curve not presented). As shown on Figure 5, the introduction of 150 phr of untreated ATH leads to a strong increase in the stress level at a given strain with an increase in the stress at break and a decrease in the strain at break, as usually observed for micron size filled composites [29, 30]. The use of the filler treatment leads to a very strong hardening during stretching. The materials with treated and untreated fillers have the same strain at break but the stress at break of E-150ATHT is much higher i.e. around 6 MPa. Thus, as said before, the presence of the filler-matrix covalent bonds is mainly evidenced at large strain, the fillers acting like multifunctional crosslinks.

The effect of filler treatment is also observed in the cycle tensile tests at 80°C (cf. Figure 6). For each incremental true strain, the cycle area, significant of the material damage, between two successive curves, is plotted versus true stress. The stress at which a same cycle area, i.e. same rupture energy, is obtained, is higher for E-CR-150ATHT-0 than for E-CR-150ATHU-0. This evidences the role of strong filler-matrix bonds created by the silane treatment which delays the material damage.

3.2. Oxidation

After the radio-oxidation of EPDM, an increase in absorbance in the hydroxyl absorption region (3800-3000 cm-1) was observed [1, 2] corresponding to the formation of alcohols, acids and hydroperoxides. The formation of carbonyl can be evidenced by an absorption

maximum at 1713 cm^{-1} accompanied by several shoulders around 1785, 1755, 1740, and 1695 cm^{-1} [1]. The measurements by IR spectroscopy (ATR) have shown that in the case of ATH filled EPDM, the same oxidation products are generated. For all materials (unfilled and filled), an increase in hydroxyl and carbonyl absorption regions can be observed with an increasing irradiation dose, but it was not possible to quantify these products by ATR and thus to compare the oxidation level of the different elastomers. Indeed, the IR beam depth penetration and the number of reflections in the samples can be influenced by the presence of fillers. Moreover, scattering phenomena can occur.

However, the use of IR - microspectroscopy on sample slice can provide the oxidation product distribution within the sample thickness. The variations in absorbance at 1713 cm^{-1} are chosen for this characterisation. For E-CR-510 and E-CR-150ATHU-510, i.e. at the maximal irradiation dose, the oxidation profiles are nearly flat; this indicates that in the irradiation conditions of this study, the oxidation processes are homogeneous within the sample thickness.

3.3. Degradation kinetic

Uncrosslinked materials: .For the E-NC material, Q and Fp decrease with irradiation dose up to 300 kGy, then stabilizes up to 510 kGy, whereas, the elastic modulus at 80°C increases and then decreases (cf. Figure 2a, 3a and 4a respectively). This evidences that this material is submitted to both phenomena of crosslinking and chain scissions. The first is preponderant at the beginning of irradiation, whereas the latter becomes preponderant at high irradiation doses. The same evolution can also be observed for E-NC-150ATHU material (cf. same figures). However, at high irradiation doses, its soluble fraction F_p is higher than the one of E-NC. In addition, its elastic modulus at high irradiation doses is closed to that of E-NC. These results strongly suggest that the matrix is more rapidly degraded in presence of fillers.

Crosslinked materials: For E-CR (Figure 2 b), between 0 and 50 kGy, no variation of Q and a slight increase in the soluble fraction F_p (Figure 3) are observed. Then for higher irradiation doses, the soluble fraction rapidly increases as well as the swelling ratio. The material filled with 32 phr of ATH presents the same evolution, with a swelling ratio slightly lower due to a small swelling restriction induced by the ATH-matrix interaction. The reinforcement factor slightly decreases from 1.2 to 1.1 with the irradiation dose. Given the measurement uncertainties, these result does not enable to conclude if the polymer degradation is identical or slightly accelerated with the presence of 32 phr of ATH.

As also seen previously with uncrosslinked materials, the irradiated E-CR-150ATHU shows an increase in the sol fraction with irradiation dose, which is more important than the one observed for unfilled matrix (E-CR) at high irradiation dose. Moreover, the modulus decrease of E-CR-150ATHU material is also more important with an increasing irradiation dose than in the case of the E-CR material. The reinforcement efficiency decreases from around 3.5 for non irradiated sample down to around 2.4 for aged samples. Thus, for crosslinked as well as uncrosslinked materials, the presence of an important fraction of ATH promotes the material degradation. This will be discussed in section 3.4.

Concerning the treated fillers, the sol fraction increases more slowly than in the case of E-CR-150ATHU. This leads at 510 kGy to the same value of the sol fraction for both E-CR-150ATHT and E-CR-150ATHU. As said above, E-CR-150ATHT is likely less crosslinked than E-CR-150-ATHU ; it is also known that the sol fraction increase due to the degradation of the material is inversely proportional to its crosslink density [5]. Therefore, within the assumption that the degradation mechanism is similar for both samples (that is with the same scission yield), one could have expected a more rapid increase in the sol fraction versus irradiation dose for the material with treated fillers. Thus, the same value of the sol fraction at 510 kGy of E-CR-150ATHU and of E-CR-150ATHT materials means (i) either that the chain

scission phenomenon is counterbalanced by some residual crosslinking reaction, induced by residual silanes which have not reacted at the polymer-matrix interface or by a crosslinking of the initially non crosslinked sol fraction by irradiation (like observed in the case of uncrosslinked EPDM under irradiation [5]), (ii) or that the filler treatment inhibits the acceleration of the degradation mechanisms promoted when the fillers are not surface treated.

In spite of a different evolution of their sol fraction, E-CR-150ATHU and E-CR-150ATHT materials show a similar evolution of their elastic modulus with irradiation dose. Whatever the radiation dose, the modulus of E-CR-150ATHT is below that of E-CR-150ATHU. As said in section 3.2, the filler treatment can promote a better filler dispersion which can lead to lower effective aspect ratio of the fillers, and therefore to a lower reinforcement. However a less rapid decrease in the elastic modulus for E-CR-150ATHT material at the beginning of irradiation can be noticed. This can be related to the quasi-constant sol fraction of this material for doses below 300 kGy, which confirms the crosslinking phenomenon at the beginning of irradiation.

3.4. Consequences on mechanical properties at 80°C at large deformations

Untreated ATH : Figures 5 present the tensile curves of the irradiated crosslinked samples. With untreated fillers, irradiation leads to a decrease in the stress at a given strain. This is obviously due to the polymer degradation. All the materials filled with untreated fillers have a totally different rupture behavior compared to the unfilled materials which show a degradation of their ultimate properties with irradiation (i.e. a decrease in both stresses and strains at break). Their elongation at break is largely increased with irradiation dose while the stress at break is kept constant. These differences in ultimate properties must be related to the possibility or not of energy dissipation provided by the fillers through decohesion mechanisms. Note that the behavior of E-CR-30ATHU, not presented here, is similar to that of E-CR-150ATHU sample except that the reinforcement is, as expected, smaller.

Treated ATH: the evolution of the tensile properties of E-CR-150ATHT with radiation dose shows two sequences. Firstly, at low dose, like for untreated fillers, irradiation leads to a decrease in the stress levels. In the same time, the elongation at break tends to decrease, as observed in the case of the unfilled matrix. Thus, the silane treatment hinders matrix decohesion, which means that at the early stage of degradation, the matrix controls the rupture properties. Secondly, at higher doses, like in the case of untreated fillers, the deformation at break increases. This could be an indication of a partial degradation of the filler-matrix covalent bonds, or at least, of the degradation of the polymer matrix in the filler vicinity, eventually enabling at high irradiation dose some decohesion mechanisms.

The decrease in the ability of the ATHT-matrix interaction to avoid decohesion with increasing irradiation can be evidenced by the results of the tensile test cycles carried out at 80°C (see Figure 6). Indeed irradiation leads to a strong decrease in the stress value at which the increase in cycle area occurs. This is evidenced for treated and untreated fillers, though this decrease is more important for treated fillers: it changes from around 5 MPa at 0 kGy down to 3 MPa at 510 kGy. Note however, that the stress level measured at a given strain for E-CR-150ATHT is still higher than that measured for untreated filler, indicating that some strong bonds between the filler and the matrix remain.

3.5. Evaluation of the filler influence on the degradation kinetic

The possibility of a more rapid degradation of the matrix in presence of filler can be quantitatively estimated from the different experimental results.

For E-CR-150ATHU: considering the modulus data, it can be made the assumption that the reinforcement factor is independent on the irradiation dose. Such assumption is reasonable since the filler dispersion, geometry and modulus is likely not modified by irradiation. Taking

a reinforcement factor F of 3.1[†] (which is the theoretical value given by the Christensen and Lo model), the evolution of the elastic modulus E_m of the polymer phase can be deduced from the experimental values of the elastic modulus of the composite material E at 80°C, (cf. Figure 7 b). It is clearly shown from the deduced curve the more rapid degradation of polymer phase in the filled materials than in the unfilled material. As shown in a previous paper [30], the evolution of the elastic modulus of the matrix during irradiation for E-CR and E-CR-150ATHU materials can be fitted above 50 kGy, following the relation:

$$E_{fit} = E_0 \left(1 - F_p\right)^{1/3} \exp\left(-ASD\right) \quad (4)$$

With D the irradiation dose, E_0 the extrapolated elastic modulus of the matrix at 0 kGy, F_p the soluble fraction, S a parameter significant of the efficiency of the dose in the scission reaction. Note that this equation is only used above 50 kGy since a simultaneous crosslinking phenomenon occurs below 50 kGy. The additional parameter A is taken equal to one for E-CR; its value in the case of E-CR-150ATHU is deduced from the curve fit. Taking all the other parameters equal to those used for E-CR, a very good fit is obtained with a factor A equal to 1.5 (cf. Figure 7 b), suggesting that the filler presence leads to a degradation kinetic 1.5 times more rapid.

Another estimation of the kinetic acceleration by the filler presence can be deduced from the sol fraction data. To do so, the Charlesby's approach is used [31, 32]. This gives a simple expression relating the sol fraction F_p to the irradiation dose. Following a previous paper [30], for E-CR material, since the major phenomenon occurring after 50 kGy is chain scission, the proportion of crosslinked monomers (q_f) can be taken as constant. Thus, the relation of Charlesby becomes affine with D:

[†] Taking a reinforcement factor of 3.5 (which corresponds to experimental data), the found acceleration of the degradation due to the filler presence would be more important than that estimated with a reinforcement factor of 3.1 and therefore our conclusion would be even reinforced.

$$F_p + \sqrt{F_p} = \frac{p_0 D}{q_f} + \frac{1}{q_f u_1} \quad with \quad u_1 = \overline{M_n} \Big/ w \quad (5)$$

The value of q_f can be estimated from the extrapolated elastic modulus of E-CR at 0 kGy (cf. Figure 7 a). It is found equal to 0.015. Moreover, in this equation, p_0D represents the chain scission kinetic. Here it is made the assumption that this kinetic is proportional to the irradiation dose (like Charlesby did in his work). Therefore p_0 is a constant. $\overline{M_n}$ and w are respectively the average number molar weight and the molar mass of the polymer unit.

As shown in the figure 8 b), the experimental evolution of $F_p + \sqrt{F_p}$ versus irradiation dose is in a good agreement with the relation (6). The value of p_0 deduced from the fit is equal to 1.67×10^{-5} kGy^{-1}. The same approach is used for E-CR-150ATHU material. Again the fit is very satisfactory. It is found a slope value of 1.7×10^{-3} kGy^{-1}. Taking for q_f the same value than for the matrix, it is found a value of p_0 equal to 2.58×10^{-5} kGy^{-1}. This is again 1.5 times the value of p_0 found for E-CR, confirming the value of the acceleration factor previously deduced from the modulus data.

***E-NC-150ATHU material**:* this case is more difficult, since these materials are submitted to an important crosslinking process during irradiation. However the evolution of the modulus of the E-NC-150ATHU matrix taking the same reinforcement factor used for E-CR-150ATHU (3.1) can be estimated. The curve deduced from a division of the composite modulus by this factor (Figure 7 a) suggests again that the crosslinking process (before 165 kGy) and the degradation (after 165 kGy) are more rapid in presence of fillers. An estimation of this acceleration by the fillers can be quantified. Following reference 5, the elastic modulus of matrix for these materials (E-NC, E-NC-150ATHU) can be fitted by:

$$E_{fit} = E_0' \left(1 - F_p\right)^{1/3} = E_0' \left(1 - F_p\right)^{1/3} \left(1 - \exp\left(-ACD\right)\right) \exp\left(-ASD\right) \quad (6)$$

With S significant of the scission kinetic and C related to the crosslinking process. A is equal to one for E-NC since it is the reference material. For E-CR-150ATHU, taking the same parameters used for E-NC, the best fit is obtained with A equal to 2. Thus the acceleration by the filler presence of the chemical processes involved by irradiation is also evidenced in the case of initially uncrosslinked materials and seems to be even more pronounced.

To conclude, all experimental results suggest that the introduction of ATH fillers in EPDM matrix increases the efficiency of the irradiation. The acceleration factor is of the order 1.5 for crosslinked materials and even higher for uncrosslinked one.

Different articles report ATH degradation under gamma or electronic irradiation [14, 15, 33]. This degradation especially leads to their dehydration and the formation of radicals. These supplementary radicals might be at the origin of the observed accelerated degradation in the composite. Same articles suggest that the supplementary radicals are localized at the filler surface. This points out that the accelerated degradation in composite should preferentially occur in the filler vicinity. The use of filler treatment could have brought supplementary information on this phenomenon. Unfortunately, as discussed previously, the E-CR-150ATHT matrix was initially less crosslinked than E-CR. This leads during irradiation to a supplementary crosslinking phenomenon, which hinders the same type of analyses performed with E-CR-150ATHU. This makes any conclusion on the role of the filler surface in the degradation process more difficult. However, if we consider the evolution of the sol fraction of E-CR-150ATHU and of E-CR-150ATHT versus irradiation dose, we can note that both join at high irradiation dose, suggesting that the crosslinling process occurring in E-CR-150ATHT at the beginning of irradiation compensates the initial lower crosslink density so that this one reaches the one of E-CR-150ATHU at high dose. Thus, at high irradiation level, the matrix in both materials composite might be similar, which would be in agreement with the evolution of the elastic modulus. Within this assumption, that would mean that the

acceleration of the degradation mechanism is similar for both materials. Such conclusion is surprising since the ATH treatment is expected to modify the formation of the supplementary radicals at their surface. This can be possibly explained by a degradation of the filler-matrix covalent bonds induced by filler treatment. However, the swelling results and the mechanical properties at large deformations imply that these interactions are not totally degraded during irradiation.

If some questions remain about the mechanisms involved in the acceleration of the degradation kinetic by the fillers, in any case this acceleration has tremendous consequences in the mechanical properties when the materials are tested above their melting temperature (60°C). The next section is focused on the consequences of the irradiation on the mechanical properties below this temperature, i.e. in the semi-crystalline state.

3.6. Consequences on the mechanical the properties at 25°C

It has been reported in a previous study [11] that our unfilled EPDM presents a lamellar microstructure in the undeformed state. In the case of ATH filled EPDM, the Small-Angle X-Ray Scattering experiments cannot be easily used because of the presence of fillers: indeed the absorption due to the fillers masks the crystallite scattering. However, DSC can still be used. The results indicate that the filler has a negligible impact on the crystalline microstructure of the matrix. Moreover, the crystallinity ratio as well as the peak temperatures of the materials are not strongly modified after irradiation: the cristallinity and the peak temperatures increase of around 1% and 5°C respectively. Thus, it can be concluded that irradiation only leads to a slight process of chemi-crystallization which does not significantly modify the microstructure of the filled materials.

Table 4 also reports the elastic modulus of non irradiated E-CR, E-CR-150ATHU and E-CR-150ATHT, deduced from the tensile tests presented in Figure 9. The semi-crystalline phase induces a strong increase in the elastic modulus and in the stress level at given strain for all the materials. The crystalline microstructure seems to control the strain at break, which is remarkably higher than that measured at 80°C for the same materials. As expected, the introduction of 150 phr of ATH leads to an important reinforcement of the material, within a ratio of 3.2. Like at 80°C, such a ratio is close to the one predicted by Christensen and Lo model [27, 28]. This suggests that there is no synergistic effect between the fillers and the crystallites in the reinforcement such as the one reported in the case of the semi-crystalline nanocomposites [10, 24]. Moreoever, the filler treatment does not have significant influence on the reinforcement at low strains. This was expected since it does not have one at high temperature, and it does not either significantly change the crystalline morphology. However, like at 80°C, the silane treatment induces an important hardening and a decrease in the strain at break. This hardening is obviously due to the filler-polymer covalent bonds which are mechanically active at large strains.

As shown in table 4 , in the case of E-CR-150ATHU, irradiation leads to in to a decrease of ca. 25% of the modulus below 300 kGy, which then stabilizes at high irradiation doses. This decrease is much lower than the one found at 80°C, indicating that the crystallites attenuate the effect of the matrix degradation. With treated fillers, the modulus evolution is within the uncertainties. The modulus stability below 300 kGy might be explained by the supplementary crosslinking phenomenon previously evidenced by the tensile tests performed at 80°C.

As shown in Figure 9, when the materials are irradiated, the presence of fillers leads to a strong increase in the stress level at intermediate strain, followed by a decrease in stress level at the highest strain (in other words to a decrease in hardening). Thus, the stress at break for E-CR-ATH150U is lower than for E-CR, and the strain at break is roughly unchanged (cf.

Table 3). This can be explained by the decohesion process already evoked in section 3.3., which leads at high strain to a lower stress level. This decohesion process seems to be more pronounced for irradiation dose above 50 kGy like previously observed at 80°C.

Given the experimental uncertainties, it is difficult to comment in detail the rupture behavior of the irradiated E-CR-150ATHT materials. However, like at 80°C, it can be noticed a slight decrease in the strain at break for irradiation dose below 300 kGy followed by a increase in this strain at break for higher irradiation dose, while the stress at break slightly decreases. As explained above, this behavior might be due to a promoted decohesion mechanism at larger irradiation dose although the development of this mechanism is limited by the silane treatment.

4. Conclusions

The addition of micronic fillers such ATH induces a reinforcement of the mechanical properties at small strain predicted by classical model. This reinforcement is similar when these fillers are treated with a coupling agent, but this treatment induces a strong hardening at large strains, below and above the melting temperature. The filler influence on the degradation mechanisms during ageing by gamma irradiation, and on the evolution of mechanical properties is clearly evidenced. Indeed, the presence of an important filler fraction accelerates the degradation. Above the melting temperature, this induces a decrease in the apparent mechanical reinforcement factor with increasing irradiation dose. In addition, with untreated fillers, the degradation promotes decohesion mechanisms which enables larger strains at break than those measured with unfilled materials. The acceleration of the degradation kinetic by the filler might be due to the formation of supplementary radicals at the filler surface; however it is not clear whether the use of the filler treatment attenuates or not this accelerating effect. Thus the mechanisms involved in the acceleration of the degradation are not yet well understood by the authors. Note that part of the filler treatment remains

efficient at high dose and seems also to delay but not suppress the occurrence of decohesion mechanisms at large strain.

Like already observed in the case of unfilled crosslinked EPDM [11] and silica filled EPDM [34], the consequences of ageing by gamma-irradiation are strongly limited below the melting temperature, because of the presence of crystallites. These crystallites can be seen as supplementary multifunctional crosslinks which are mechanically more active than the elastomer crosslinks. Therefore the inactivation of the polymer crosslinks by chain scission mechanism is made less important in the material mechanical response and all the phenomena evidenced above the melting temperature are partially masked in the semi crystalline state.

To conclude, this paper highlights that the filler presence has an influence on the degradation mechanism and that the consequences of this degradation on the composite mechanical properties are not straightforward. Thus it seems obvious that it is not possible to understand and deduce the evolution of the mechanical properties of filled composite submitted to irradiation from the sole study of the degradation of the unfilled polymer.

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